FIELD-ACTIVATED COMBUSTION SYNTHESIS OF CERAMIC AND COMPOSITE MATERIALS

FINAL PROGRESS REPORT

Z.A. MUNIR

AUGUST 10, 1998

U.S. ARMY RESEARCH OFFICE

DAAH04-95-1-0253

UNIVERSITY OF CALIFORNIA, DAVIS

MASTER COPY KEEP FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
8-10-98

3. REPORT TYPE AND DATES COVERED
Final Report

4. TITLE AND SUBTITLE
Field-Activated Combustion Synthesis of Ceramic and Composite Materials

5. FUNDING NUMBERS
DAAH04-95-1-0253

6. AUTHOR(S)
Z. A. Munir

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
University of California
Davis, CA 95616

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 34389.16-MS

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
Modeling and experimental investigations on the effect of an electric field on the synthesis of materials by the self-propagating combustion method were carried out. The aim of these investigations included: (a) providing a fundamental understanding of the role of the field in synthesis, (b) simultaneously synthesizing and densifying hard materials, (c) synthesizing materials from highly dense reactants, and (d) determining the role of the field in the microstructural developments during synthesis.

14. SUBJECT TERMS

15. NUMBER IF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 3

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18

FIELD-ACTIVATED COMBUSTION SYNTHESIS OF CERAMIC AND COMPOSITE MATERIALS

FINAL PROGRESS REPORT

Z.A. MUNIR

AUGUST 10, 1998

U.S. ARMY RESEARCH OFFICE

DAAH04-95-1-0253

UNIVERSITY OF CALIFORNIA, DAVIS

Forward:

The continuing drive to satisfy the demand for high performance materials focuses on innovative approaches to produce new materials with the desired properties, or to improve existing materilas through creative processing by compositional or microstructural modifications. Among these approaches is the use of self-propagating high-temperature combustion to synthesize and process new materials, including monolithic and composite materials. The more recent use of an electric field to activate such a synthesis method was aimed at influencing the mechanism of synthesis (and hence the nature of the products) and at influencing the microstructural development of the product. Significant success has been achieved in both of these directions over the past three years, with encouraging results on high temperature and hard materials of special interest to ARO.

Statement of the Problem Studied:

The broad aim of the research undertaken was to investigate the role of an electric field in the synthesis of materials by the self-propagating combustion method. The specific objectives were to (a) provide an understanding of the role of electromagnetic fields in the synthesis and processing of materials, (b) utilize the field to synthesize new materials, (c) to simultaneously synthesize and densify materials, (d) synthesize by SHS from dense reactants, and (e) investigate the influence of the applied field on microstructural development during synthesis. The ultimate goal is to use the field as a *processing parameter in the synthesis of materials.*

Summary of the Most Important Results:

A. Synthesis of Nitride Composites and Solid Solutions

The proposed use of AlN-SiC composites in high performance spark plugs motivated the investigation of synthesizing by field activated SHS from Si_3N_4, C, and Al. Through field application it was possible to form composites and solid solutions. The compositions of the phases in the composites were directly dependent on the value of the applied field, and the uniformity of the elemental distribution in the solid solutions could be directly influenced by the field. The significance of field activation can be seen by realizing that solid solutions made by conventional methods involve tthe heating of AlN and SiC at high temperatures ($\approx 2100°C$) for long periods of time (up to 16 hrs). With field-activated SHS, the solid solutions can be made in seconds. Details of these accomplishments are given in items 1 and 2 in the list of publications, below.

B. Simultaneous Synthesis and Densification

In order to maximize the benefits of the field activation method, a new modification was utilized to effect the simultaneous synthesis and densification of materials. Our effort in this area of investigation has been equipment-limited. The recently awarded DURIP proposal will alleviate this problem and will make possible the simultaneous synthesis and densification using a modified field-activated combustion synthesis. The US Patent Office has recently approved a patent disclosure on our method and the patent is expected to be issued by the end of summer. With the DURIP award, an order has been placed for a "spark-plasma synthesis" machine. It is anticipated that this equipment will be in operation by early fall. In the meantime, we have put together a temporary apparatus to investigate this method of synthesis and densification. The few preliminary results we have obtained with this apparatus have been encouraging. They include (a) the synthesis from the elements of 99% dense $MoSi_2$, (b) the synthesis of $MoSi_2$-WSi_2 solid solutions from

elemental reactants, and (c) the synthesis of materials in the ternary Mo-Si-Al. We have succeeded in synthesizing single phase (C40) $MoSi_{2-x}Al_x$, with $0.4 \leq x \leq 1.0$ using field-activated SHS and the modified method mentioned above. In the latter, we have synthesized the C40 phase with densities as high as 99.3%. The ultimate goal of this phase of our research is to synthesize and characterize dense hard materials of interest to ARO.

C. The Synthesis and Densification of a New Class of Ternary Materials:

An important focus of the research to be carried out under the renewal of the current proposal is the synthesis of ternary materials such as Ti_3SiC_2 and H-phases (e.g., Ti_2AlC). The Ti-Si-C ternary has attractive properties, which combine those of a refractory ceramic with a metallic-like toughness. Our preliminary work, using an interim apparatus shows that we can synthesize this ternary with a grain size smaller than in any of the previously reported investigations. The smaller grain size is a consequence of the lower temperature and shorter reaction time in our modified field-activated combustion synthesis. Preliminary characterization of this material through mechanical, chemical, and physical evaluations have been recently made. However, major emphasis on this phase of our research will be made after the installation of the equipment ordered with the DURIP grant.

D. Initiation of SHS Waves in Dense Powder Reactants:

This phase of our work was part of a collaborative effort with Professor Thadhani at Georgia Tech using the synthesis of molybdenum silicide as a model system. The general aim of this work is to reduce the final porosity of SHS products by using dense powder reactants. The work has been recently comleted and a paper has been submitted recently (see item #14) in the publication list). As indicated in the interim progress report, Mo + 2Si reactants with relative densities of ≥ 78% cannot be ignited by the usual SHS method. But under the influence of an electric field, SHS waves can be initiated in powders with relative densities as high as 95%. The measured dependence of the wave velocity on relative density is consistent with other observations, and in this case is explained in terms of the role of a liquid phase in the synthesis of this silicide, as discussed in more detail in the submitted paper.

E. Effect of Field on Microstructural Developments in SHS Synthesis:

The imposition of a field increases the temperature and velocity of the combustion wave. These observations give rise to expectation of a steeper temperature gradient on the receding end of the wave, and hence to the minimization of grain growth during SHS synthesis. Preliminary investigations were made on the effect of a field on the grain size of $MoSi_2$. The results show a decrease in the grain size with increasing field strength up to a field value corresponding to a combustion temperature equivalent to the melting point of the product. These results have been described in a paper given at a TMS symposium whose proceedings are in press (see item #9 in the publication list).

Publications and Presentations:

a. Published and Submitted Papers

1. H. Xue and Z. A. Munir, "The Synthesis of Composites and Solid Solutions of Alpha SiC- AlN by Field Activated Combustion," *Scripta Metallurgica et Materialia*, **35**, 979-982 (1996).

2. H. Xue and Z. A. Munir "Synthesis of AlN-SiC Composites and Solid Solutions by Field-Activated Self-Propagating Combustion," *J. Euro. Ceram. Soc.*, **17**, 1787-1792 (1997).
3. A. Feng and Z. A. Munir, "The Effect of Product Conductivity on Field-Activated Combustion Synthesis," *J. Amer. Ceram. Soc.*, **80**, 1222-1230 (1997).
4. Z. A. Munir, "Electrically-Stimulated SHS," *Int. J. SHS*, **6**, 165-185 (1997).
5. Z. A. Munir, "Field Effects in Self-Propagating Solid-State Synthesis Reactions," *Solid State Ionics*, **101**, 991-1001 (1997).
6. I. J. Shon and Z. A. Munir, "Synthesis of TiC and TiC-Cu Composites and TiC-Cu Functionally Graded Materials by Electrothermal Combustion," *J. Amer. Ceram. Soc.*, in press, 1998.
7. S. Gedevanishvili and Z. A. Munir, "An Investigation on the Combustion Synthesis of $MoSi_2$-β SiC Composites through Electric Field Activation," *Mater. Sci. Eng.*, **A242**, 1-6 (1998).
8. I. J. Shon and Z. A. Munir, "Electric Field Activated Combustion Synthesis of Ti_5Si_3-x Nb and Ti_5Si_3-y ZrO_2 Composites," *J. Mater. Sci.*, **32**, 5805-5810 (1997).
9. Z. A. Munir, "Synthesis of $MoSi_2$ and $MoSi_2$ Composites by Field-Activated Combustion," Proceedings of the Symposium on Molybdenum and Molybdenum Alloys, TMS Annual Meeting, San Antonio, TX, February 16-18, 1998, in press.
10. Z. A. Munir, "Field-Activated Synthesis of Composites," Proceedings of the Fourth International Conference on Ceramic-Ceramic Composites," Mons, Belgium, November 18-20, 1997, in press.
11. M. Ohyanagi, N. Balandina, K. Shirai, M. Koizumi, and Z. A. Munir, "Synthesis of AlN-SiC Solid Solutions by Combustion Nitridation," Proceedings of Symposium on Innovative Processing and Synthesis of Ceramics, Glasses, and Composites, Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 4, 1998, in press.
12. H. Xue, M. Ohyanagi, and Z. A. Munir, " Reactive Synthesis and Phase Stability Investigations in the System AlN-SiC," *J. Amer. Ceram. Soc.*, submitted, 1998.
13. A. Feng, T. Orling, and Z. A. Munir, "Field-Activated Pressure-Assisted Combustion Synthesis of Polycrystalline Ti_3SiC_2," *J. Mater. Res.*, submitted, 1998.
14. H. Xue, K. Vandersall, E. Carrillo-Heian, N. N. Thadhani, and Z. A. Munir, "Initiation of Self-Propagating Combustion Waves in Dense Mo + 2Si Reactants through Field-Activation," *J. Amer. Ceram. Soc.*, submitted, 1998.

(b) Presentations:

1. Z. A. Munir, "Synthesis of Nitride Phases by Field-Activated Combustion," International Symposium on Nitrides, St. Malo, France, May 28. (Invited Speaker)
2. Z. A. Munir, "Field Effects in Self-Propagating Solid-State Synthesis Reactions," XIII International Symposium on the Reactivity of Solids, Hamburg, Germany, September 9-12, 1996. (Invited Key Speaker).
3. Z. A. Munir, "Field-Activated Synthesis of Ceramics and Composites," Insitut fuer Material Forschung, GKSS Forscungszentrum, Geesthacht, Germany, September 13, 1996. (Invited Seminar).
4. Z. A. Munir, "Synthesis of Nitride Composites by Field-Activated Combustion," Symposium on Processing and Fabrication of Advanced Materials, TMS Materials Week '96, October 7-11, 1996, Cincinnati, OH. (Invited Paper)
5. Z. A. Munir, "Field-Acivation Of The Combustion Synthesis Of Ceramics And Composites," Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH, October 11, 1996. (Invited Seminar)

6. Z. A. Munir, "The Synthesis Of Aln-Sic Composites And Solid Solutions By Field-Activated SHS," Department of Materials Chemistry, Ryukoku University, Otsu, JAPAN, October 24, 1996. (Invited Seminar)
7. Z. A. Munir, "The Use Of An Electric Field As A Processing Parameter In Combustion Synthesis," Department of Metallurgy and Materials Science, University of Tokyo, Tokyo, JAPAN, October 25, 1996. (Invited Seminar)
8. Z. A. Munir, "Synthesis And Processing Of Ceramics, Composites, And Intermet-Allics By Field-Activated Combustion," Symposium on Advances in Synthesis and Processing of Metal and Ceramic Matrix Composites, TMS Annual Meeting, Orlando, FL, Feb. 9-13, 1997. (Invited Paper)
9. Z. A. Munir, "Synthesis And Densification By Field-Activated SHS," Department of Materials Chemistry, Ryukoku University, Otsu, JAPAN, July 2, 1997. (Invited Seminar)
10. Z. A. Munir, "Self-Propagating High-Temperature Synthesis: An Overwiew," Dedication Ceremony for the High-Tech Research Center, Ryukoku University, Otsu, JAPAN, July 4, 1997. (Invited Presentation)
11. Z. A. Munir, "The Influence Of An Electric Field On Materials Synthesis By Self-Propagating Combustion," Department of Chemical Engineering , Unioversity of Cagliari, Cagliari, ITALY, September 12, 1997. (Invited Seminar)
12. Z. A. Munir, "Elecrically-Stimulated SHS," Fourth International Symposium on Self-Propagating High-Temperature Synthesis, Toledo, SPAIN, October 6-10, 1997. (Invited Plenary Lecture)
13. Z. A. Munir, "Field-Activated Combustion Synthesis Of Composites," Fourth International Conference on Ceramic-Ceramic Composites, Mons, BELGIUM, November 18-20, 1997. (Invited Keynote Paper)
14. Z.A. Munir, "The Synthesis Of High Temperature Materials By Field-Activated Self-Sustaining Combustion," Institut für Gesteinshüttenkunde, Rheinische-Westfalische Technische Hochschule, Aachen, GERMANY, November 21, 1997. (Invited Seminar)
15. M. Ohyanagi, T. Hiwatashi, M. Koizumi, and Z. A. Munir, "Combustion Synthesis of AlN-SiC Solid Solutions,", 49th Pacific Coast Regional Meeting of the American Ceramic Society, San Francisco, October 12-15, 1997.
16. A. Feng and Z. A. Munir, "Field-Activated And Presure-Assisted Synthesis of Ti_3SiC_2", 49th Pacific Coast Regional Meeting of the American Ceramic Society, San Francisco, October 12-15, 1997.
17. R. Orru, Z. A. Munir, and G. Cao, "Combustion Synthesis Of Titanium Aluminides Assisted By An Electric Field," 1997 Annual Meeting of the AIChE, Los Angeles, November 16-21, 1997.
18. Z. A. Munir, "The Synthesis of $MoSi_2$ and $MoSi_2$-Composites By Field-Activated Combustion," Symposium on Molybdenum and Molybdenum Alloys, TMS Annual Meeting, San Antonio, TX, February 16-18, 1998. (Invited Paper)
19. Z. A. Munir, "Synthesis of Hard Materials By SHS", Magotteux International Company, Liege, BELGIUM, April 22, 1998. (Invited Seminar)

Participating Scientific Personnel:

Z. A. Munir, Professor and Principal Investigator
A. Feng, Postdoctoral Fellow; currently, Research Engineer, Read-Rite Corporation, Fremont, CA 94539.
H. Xue, MS and PhD student; currently, Research Engineer, Integrated Device Technology, Inc., Santa Clara, CA 95052.
Tim Olring, PhD Student.